g, 77%) after evaporation of the solvent, ir (CCl_4) 2120 (N_3), 1750 1770 (C=O), 690 cm^{-1}.

The infrared spectrum of the product was identical with that of diethyl azidophenylmalonate prepared from diethyl bromophenylmalonate and sodium azide according to a published procedure.[18]

Diethyl Azido(7-cycloheptatrienyl)malonate (IIb). A procedure similar to that used in the synthesis of the azidophenylmalonate was employed, starting with 5.29 g (0.021 mol) of diethyl (7-cycloheptatrienyl)malonate.[19] The usual work-up procedure yielded 3.80 g (65%) of a yellow oil, ir (CCl_4) 2120, 1750, 1740, and 700 cm^{-1}.

The crude product was purified by chromatography on activated alumina and eluted with benzene–hexane (1:3), nmr (CCl_4) δ 1.30 (t, 6 H), 2.19 (t, 1 H), 4.20 (q, 4 H), 5.20, 6.15, 6.60 (m, 6 H).

9-Carbomethoxy-9-azidofluorene (IVa). The sodium salt of 9-carbomethoxyfluorene (2.80 g, 0.0125 mol) was prepared from reaction with sodium hydride as described above. To the brown solution of the anion was added dropwise a solution of 2.46 g (0.0125 mol) of tosyl azide in glyme at room temperature, and the reaction mixture was then heated under reflux for 2 hr. After having been cooled to room temperature, it was poured into ice water and extracted with ether. The dried ethereal extract was then evaporated *in vacuo* to give a pale yellow oil which crystallized on standing. Upon filtration and washing with petroleum ether, 1.90 g (57%) of colorless crystals of essentially pure product, mp 76–78°, were isolated, ir 2100 (N_3), 1740–1710 cm^{-1} (CO_2CH_3). An analytical sample was obtained by recrystallization from petroleum ether, mp 80–81°.

Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.86; H, 4.21; N, 15.68.

α-Azidodiphenylacetonitrile (IVb). The procedure was essentially identical with that described for IVa. The dark red oil obtained was refluxed with *petroleum ether* for 1 hr and the extract was decanted from the insoluble residue. Evaporation gave a red oil which was chromatographed on Florisil, using *petroleum ether* as eluent. A second chromatography of the second fraction gave 0.92 g (18%) of pure product, mp 40–42° (lit.[20] mp 41°), ir 2170 (CN), 2170 cm^{-1} (N_3).

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Registry No.—Ia, 28744-77-6; Ib, 51157-37-0; IIa, 51065-36-2; IIb, 51157-38-1; IIIa, 51065-38-4; IIIb, 51065-37-3; IVa, 51065-39-5; IVb, 51065-40-8; tosyl azide, 941-55-9.

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(16) Other products were formed during this reaction. With methyllithium as the base, a compound analyzing for $C_{15}H_{13}N_3$ was isolated. In the case of sodium hydride, an orange compound corresponding to $C_{28}H_{21}N_3$ was isolated in good yield. The structures of these two by-products remain unclear at this time.
(17) All melting points are uncorrected. Infrared spectra were recorded in solution (CCl_4) or potassium bromide pellets; nmr spectra were recorded as solutions in deuteriochloroform, using TMS as an internal standard.
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Cleavage of δ-Keto β,γ-Unsaturated Esters by 1,4-Diazabicyclo[2.2.2]octane

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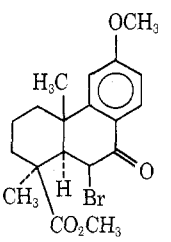
As a result of a continuing study into the improvement of the yield of lactone **2** from bromo ketone **1** by utilizing a variety of bases[4-6] we now wish to report that 1,4-diazabicyclo[2.2.2]octane (Dabco) is useful for the cleavage of δ-keto β,γ-unsaturated esters to their corresponding α,β-unsaturated ketones.



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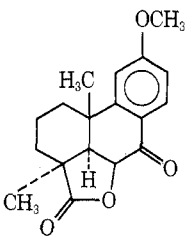

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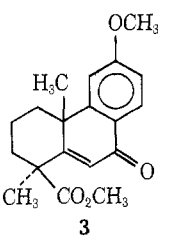

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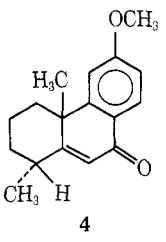

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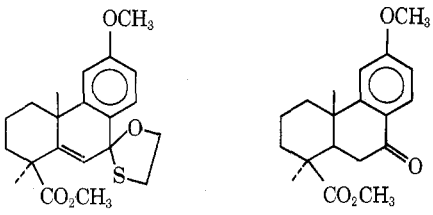
Bromo ketone **1** was reacted with 6 equiv of Dabco in 16 equiv of *o*-xylene at reflux (165°) for 6 hr. Fractional crystallization of the product mixture gave compound **4** in 80% yield and compound **2** in 10% yield. Compounds **2** and **4** were identical by ir, nmr, glc retention time, and mixture melting points with authentic samples.[4,5] Thus this reaction did produce some of the desired lactone **2** in contrast to the bases 1,5-diazabicyclo[4.3.0]nonene-5 (DBN)[4] and 1,5-diazabicyclo[5.4.0]undecene-5 (DBU).[5] However, the major component was the decarbmethoxylation product **4**. When the proposed intermediate **3** was treated with Dabco under the conditions previously described, a high (90%) yield of decarbmethoxylation product was obtained.

Since the bases DBN and DBU are *O*-alkyl cleavage reagents,[4,5] Dabco was allowed to react with esters **5**–**8** to determine if similar results could be obtained. The fact that no reaction occurred eliminates the possibility that Dabco is an *O*-alkyl cleavage reagent and indicates that this reagent cleaves δ-keto β,γ-unsaturated esters selectively.

The generality of Dabco as a reagent for cleaving δ-keto β,γ-unsaturated esters is demonstrated by the application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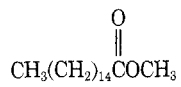
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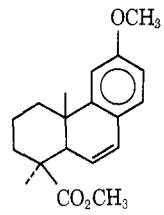
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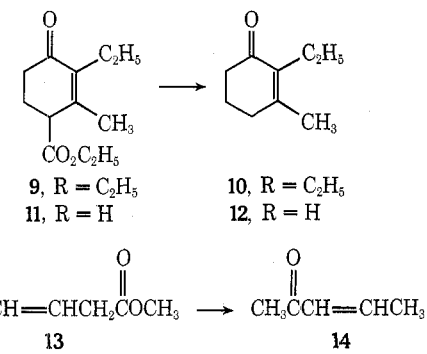
of this reagent to the esters shown in Scheme I. A mixture of 6 equiv of Dabco and 1 equiv of the appropriate ester was dissolved in 16 equiv of *o*-xylene and refluxed (165°) for 6 hr. The resulting olefins were obtained in approximately 98% yield by glc analysis and were identical by ir, nmr, and gc–mass spectral comparison with authentic samples.

Scheme I



The facile cleavage of ethyl and methyl δ-keto β,γ-unsaturated esters with a reagent (Dabco) that does not cleave saturated esters by either the *O*-alkyl cleavage or hydrolytic routes suggests that a mechanism similar to that reported by Krapcho and Lovey[7] for the cleavage of β-keto esters with sodium chloride and DMSO is probably operative.

Experimental Section

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained using a Jeolco Minimar spectrometer. Tetramethylsilane was used as an internal standard. Infrared spectra were obtained using a Perkin-Elmer Model 137 G spectrophotometer. Gas–liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 0.25 in. o.d.) bent in a U shape and packed with 3% SE-30 on 100/120 mesh GCQ at a column temperature of 270° with a helium flow rate of 90 ml/min was used for all glc analyses.

Dehydrobromination–Decarbmethylation of Bromo Ketone 1. Bromo ketone **1** (500 mg, 1.27 mmol) was added to a solution of 1,4-diazabicyclo[2.2.2]octane (Dabco, 856 mg, 7.62 mmol) and 2.42 ml of *o*-xylene. The reaction was allowed to reflux at 165° for 6 hr. The ether extract of the acidified (5% HCl) reaction mixture was washed with 5% aqueous sodium carbonate solution, dried over anhydrous sulfate, and evaporated *in vacuo*. Fractional crystallization of the residue from 20:1 methylene chloride–methanol yielded 318.5 mg (80%) of a white, crystalline compound **4** and 24.7 mg (10%) of white, crystalline compound **2**. Compounds **2** and **4** were identical by ir, nmr, glc retention time, and mixture melting points with authentic samples.

General Procedure for the Decarbalkylation of δ-Keto β,γ-Unsaturated Esters. δ-Keto β,γ-Unsaturated Keto Esters 5–9, 11, and 13. A solution of Dabco (1.712 g, 15.24 mmol) and 2.54 mmol of the appropriate ester was dissolved in 4.85 ml of *o*-xylene and the resulting mixture was allowed to reflux at 165° for 6 hr. The usual work-up of the acidified reaction mixture yielded the corresponding ketone, which was identical by ir, nmr, glc retention time, and mixture melting points with an authentic sample.

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Registry No.—**1**, 37931-64-9; **9**, 51051-65-1; **11**, 487-51-4; **13**, 51051-66-2; Dabco, 280-57-9.

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Solventless Preparation of Hydroquinone Clathrates

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The hydroquinone clathrates have long been recognized for their unusual physicochemical properties.[1] Structurally, these materials consist of two interpenetrating three-dimensional hydrogen-bonded networks of hydroquinone that enclose a set of cavities capable of accommodating a variety of small molecules such as O_2, N_2, CH_4, HCl, SO_2, Ar, Kr, etc. The composition of these clathrates is generally dependent upon the pressure and temperature conditions under which the material is formed, with the upper limit being one molecule of "guest" for every three molecules of the "host," hydroquinone. However, once the clathrate is formed, the materials remain stable under conditions far removed from thermodynamic equilibrium. For example, Peyronel and Barbieri[2] report the pressure required to produce the composition $CH_4 \cdot 3C_6H_4(OH)_2$ as approximately 100 atm at 22–30°. The structure is stable, however, at ambient conditions.

Many technological applications have been suggested for these clathrates,[3,4] but realization of their potential has, in part, been hampered by the inconvenience usually associated with the methods of their preparation. Generally, the hydroquinone clathrates have been prepared by precipitation from alcohol solutions. Resistance to mass transport by the intervening liquid phase generally requires that the clathrates be precipitated slowly, with time periods of days to weeks not being uncommon.[5] Furthermore, the tendency for hydroquinone to undergo oxidation in solution presents the risk of introduction of impurities into the crystalline product when the solution growth method is used.

Past experience with crystal growth by chemical vapor deposition methods leads us to believe that the hydroquinone clathrates might be prepared by direct reaction between the guest and host materials. The advantages to such an approach are obvious; the intervening liquid phase with its attendant mass transfer resistance is removed from the system, and continuous production, as opposed to batch production, is more readily attainable.